



## For Reference

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NOT TO BE TAKEN FROM THIS ROOM

THE DIRECT OXIDATION OF GASEOUS HYDROCARBONS  
AT HIGH PRESSURE.

by

S. N. Naldrett B. Sc.

University of Alberta,  
Edmonton, Alberta.

April, 1938.

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THE DIRECT OXIDATION OF GASEOUS HYDROCARBONS  
AT HIGH PRESSURE.

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A Thesis submitted in fulfilment of the requirements  
for the degree of Master of Science.

by

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under the direction of Dr. E. H. Boomer.

University of Alberta.

Edmonton.

April 1938.



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## I N T R O D U C T I O N

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Paraffin hydrocarbons of low molecular weight are available in tremendous quantities, and the problem of their utilization has not yet been solved satisfactorily.

The problem of transportation limits the use of these gases as fuels. The possibility of chemical conversion to useful liquid products, easily transportable, offers a field of investigation.

The most promising reactions of hydrocarbons from the point of view of economic investigations, may be classified as follows:

1. Pyrolysis.
2. Halogenation.
3. Oxidation.

Pyrolysis of the lower homologues of the gaseous hydrocarbons requires high temperatures. However, as the molecular weight increases, cracking takes place at successively lower temperatures. The ultimate products of pyrolysis are carbon black and hydrogen or water. Controlled pyrolyses will yield acetylene, olefines and aromatics, to the extent of 12 per cent or so of the methane. The process is not economical, but is sometimes used as a .



source of hydrogen.

The higher homologues of the gaseous paraffins may be pyrolyzed readily to form olefines as one of the main products. These olefines can be polymerized either simultaneously or individually to produce naphthenes, aromatics and other high molecular weight hydrocarbons. The largest percentage of the olefines are at present polymerized to produce motor fuels, and low boiling point hydrocarbon fractions, which are used as solvents in the chemical industries. .

Perhaps the greatest success in the manufacture of chemical compounds from natural gas has resulted from chlorination. The commercial preparation of monochloro-methane is now being carried out successfully. This compound may be hydrolysed to produce methanol, but it is also of use itself, as a refrigerant, and in the dye stuff industry. Other chlorination products such as chloroform and carbon tetrachloride can be made, but not cheaply enough as yet, to compete with other established methods for preparing them. Various chlorinated derivatives of pentane have been made on a commercial scale, usually with subsequent conversion to amyl acetate, for use as a solvent.

Oxidation is a promising reaction in view of the



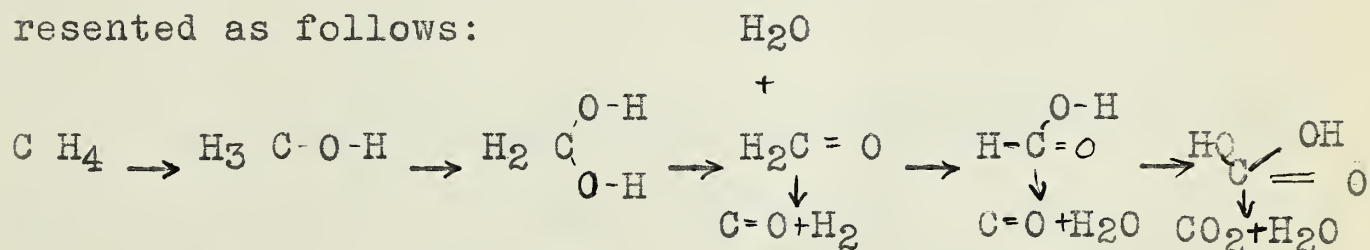
number of reactions possible, and the variety of useful products such as alcohols, aldehydes, acids and resins that may be produced. Investigations have been made not only with a view to improving the yields of useful products, but also with a view to obtaining information regarding the mechanism of oxidation of hydrocarbons. The results of previous investigations are reviewed briefly in the following section.





The most important and comprehensive investigation has been carried out by Bone and various collaborators, since about 1900. From results of his early investigations, (2) Bone proposed the "Hydroxylation Theory" of the course of the oxidation of hydrocarbons. According to this theory, the hydrocarbon molecule is oxidized in a series of consecutive operations, in which oxygen is gradually introduced into the molecule, and distributed between carbon and hydrogen. The stages may be represented as follows:

$H_2O$

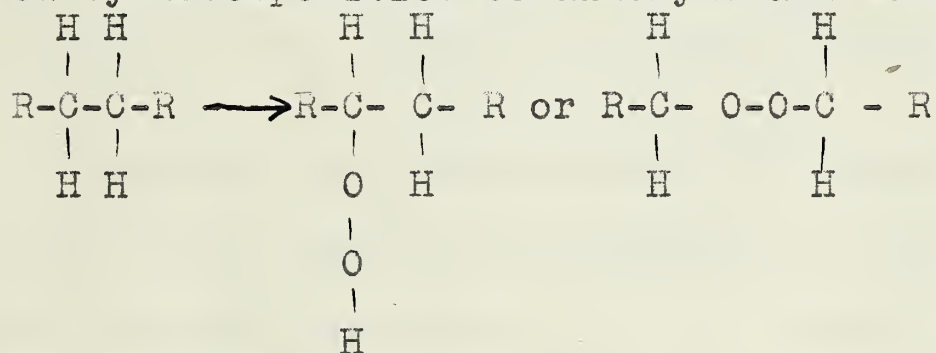


The early researches did not provide much evidence for the Hydroxylation Theory. Bone and Drugman (3) found water and formaldehyde among the first oxidation products of methane, below its ignition point. Methanol, the primary product postulated by the Hydroxylation



Theory, was not found. Bone and Wheeler(4) obtained considerable quantities of formaldehyde, with water and a small amount of formic acid, which provided further evidence for the hydroxylation theory. No methanol could be detected however.

A characteristic of all direct oxidation experiments on methane and other gaseous hydrocarbons, at atmospheric pressure, is the production of aldehydes. To explain this, certain investigators postulated the initial formation of a peroxide, by the direct addition of an oxygen molecule to a hydrocarbon molecule, followed by decomposition to aldehyde and water, thus:



The peroxide theory has received considerable support in the past, but the evidence for it has all been obtained from investigations of the combustion of higher hydrocarbons. Callender (12), Brunner and Rideal(11) and Dumanois (14) favor this theory in connection with the combustion of gasoline hydrocarbons.



Egerton (16) believes in the formation of a temporary peroxide, which can decompose to form aldehyde and water molecules, these product molecules being in a high energy state, and able to activate other fuel molecules or oxygen molecules, and so initiate a reaction chain.

Edgar (15) in studying the oxidation of octanes and similar hydrocarbons, found evidence for peroxide formation doubtful; neither did Edgar find evidence of alcohol formation. At least for these higher hydrocarbons, the results suggested that oxidation to aldehyde and water is the primary step; each succeeding step consisting of the oxidation of the aldehyde to the next lower aldehyde, with formation of carbon dioxide.

Thompson and Hinshelwood (24) suggest that while "the first stage of the reaction is the formation of an unstable peroxide----- there is no doubt that Bone's interpretation of the complete course of oxidation as a process of successive hydroxylation is essentially correct." and that "the two views are not incompatible, and a combination of them suggests an explanation of the facts."

However, in no case has evidence of peroxide formation been obtained before the formation of aldehydes, towards the end of the induction period. The appearance of







peroxides concomitant with aldehydes is of less significance, because aldehydes form peroxides fairly readily. Furthermore, peroxides have not been found at all in investigations carried out on simple hydrocarbons.

For these reasons, Bone is rigidly opposed to the theory that peroxides are formed as an initial step in the combustion of hydrocarbons, at least with respect to the lower members.

Further evidence for the Hydroxylation Theory was provided by Layng and Sonkup (17) who oxidized methane in the presence of oxides of nitrogen, and obtained small quantities of methanol, the primary product in Bone's Hydroxylation Theory. Catalysts such as copper, silver, oxides of these metals, barium oxide, platinum oxide and activated charcoal, all proved unsatisfactory on the basis of hydrocarbon consumed and products obtained. Small amounts of nitrogen oxide were found to promote the oxidation reaction. Auxiliary catalysts used with the nitrogen oxide appeared to have little effect. Methyl nitrite was found to have a promoting action on the partial oxidation of hydrocarbons.

Bibb and Lucas (/) obtained fair yields of formaldehyde in the partial oxidation of natural gas by air, using nitric acid as a catalyst.

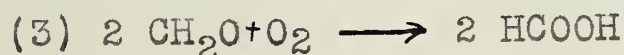
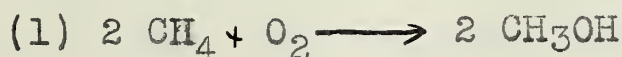


None of the oxidation processes at atmospheric pressure have resulted in production of appreciable quantities of methanol. Cristesco (13) has reported a process at atmospheric pressure, and relatively low temperature, giving large yields of methanol by the oxidation of methane. The procedure described consists of bubbling gas mixtures through boiling water, containing submerged catalysts. Yields as high as 57% are reported, upon passage of a mixture of three parts air to one methane, through the apparatus containing lead oxide, with copper oxide as supplementary catalyst.

Good yields of ethanol are reported, using a gas mixture of carbon monoxide and hydrogen. An attempt to duplicate the results was unsatisfactory. (23)

On the whole, investigations have shown conclusively that yields of methanol or formaldehyde of commercial interest, cannot be obtained at atmospheric pressure.

Writing the reactions of Bone's Hydroxylation theory stoichiometrically, it is seen that methanol and formic acid are produced with a decrease in volume, whereas formaldehyde involves an expansion:







Hence, the effect of increasing the pressure in the reacting system would be to favor the survival of methanol and formic acid, at the expense of the formaldehyde. For the purpose of raising the yield of methanol in this way, and also to obtain further information into the oxidation mechanism of hydrocarbons, work at high pressures was initiated by various investigators.

Yoshikawa (26) investigated the pressure range 12 to 100 atmospheres, using a flow method. He found an increase in pressure favored survival of methanol.

Newitt and Haffner (18) using a static method, obtained small yields of methanol. The effect of increasing the pressure from 48 to 150 atmospheres was to increase: (1) the rate of reaction for any given temperature, (2) the amount of methanol and formaldehyde in the product, and (3) the ratio of methanol to formaldehyde in the product.

Pechler and Reder (21) carried out a series of flow experiments at 100 atmospheres pressure, using various concentrations of oxygen. Yields of alcohol based on total carbon burned were as high as 22.3%.

Newitt and Szego (19) carried out a systematic investigation, with the object of discovering the order





of formation of various oxidation products, and the optimum conditions for their survival. A flow method was used, and the temperature, pressure, rate of flow and oxygen concentration adjusted to obtain the optimum survival of useful products. Pressures up to 50 atmospheres, and temperatures between 290 degrees C. and 340 degrees C., were examined. Investigations were made on methane and on ethane. By diminishing the inlet oxygen concentration, the yield of alcohol was raised to 50% of the methane burned, or to 60% of the ethane burned. No unsaturates nor peroxides were found.

These experiments and those of other investigators, demonstrated that a low oxygen concentration is necessary for good yields of useful products.

Boomer and Broughton (6) passed mixtures of oxygen and natural gas, at pressures from 100 to 180 atmospheres, and at various temperatures between 300 and 350 degrees, over various catalysts. The production of methanol, with small amounts of formaldehyde and formic acid was observed. Yields of these three products as high as 37% of the carbon oxidized were obtained. With an empty steel reactor of reaction space 7.5 cc, the oxidation proceeded rapidly and to completion, giving carbon oxides and water. Using oxide catalysts in the



reactor, barium peroxide, vanadium pentoxide or blue tungstic oxide, gave no appreciable yields of useful products. Copper and silver were more efficient in the production of methanol, but these two cannot be compared since the forms of the catalysts were different.

Wiezewitch and Frolich (25) oxidized under pressure various natural gases with oxygen, in contact with various catalysts, and determined the optimum conditions for the survival of useful products. They found that yields were high only if oxygen concentration was low. Metallic catalysts, e.g. calcium, chromel, silver and aluminum gave better results than empty tubes.

Boomer and Thomas (7) passed mixtures of natural gas, substantially methane, and air in various proportions, over catalysts and determined the effects of the variables, composition, pressure, temperature and space velocity. Mixtures containing 3 to 15% oxygen as air were used. Temperatures between 350 degrees and 500 degrees, pressures between 140 and 230 atmospheres, were examined. Methanol was the principal product and yields as high as 74% on the basis of carbon oxidized were obtained. Copper was the principal catalyst used. They concluded that the yield of useful products depends primarily on the catalyst, the oxygen concentration,





and the temperature. The effect of time of reaction and of pressure, within the limits studied, was small. They concluded that the action of the catalyst was two fold: (1) to provide a surface easily oxidized and reduced and (2) to aid in the dissipation of the heat of the reaction. They believed gas phase reactions and lack of temperature control to be detrimental.

Boomer and Thomas (8) carried out similar investigations using mixtures of pure methane containing some nitrogen, and oxygen. As for the experiments on natural gas, survival of useful products decreased as oxygen concentration was raised. The percentage of carbon oxidized showed a maximum, and the yield of useful products began to fall off rapidly, at about 6% oxygen.

The effect of pressure was not the same as for natural gas, for which it had little effect between 140 and 230 atmospheres. With pure methane, the yield passed through a maximum at 184 atmospheres pressure, for low oxygen concentrations; for high oxygen concentrations pressure had little or no effect. Temperature showed a maximum yield at about 450 degrees C. The effect of rate of flow was not significant over the range examined. The above observations were made using a copper catalyst.

Experiments were also made using an empty reactor,



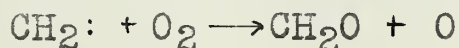


and catalysts of glass, Ni-Cr steel, and silver. As for natural gas, the yields using an empty reactor were poor, and varied erratically. Glass was as good a catalyst as copper, which was not expected because the poor heat conductivity of glass would make temperature control poor. It was suggested that the reaction took place on the copper walls of the reactor, and the glass acted merely to suppress undesirable gas phase reactions. Ni-Cr steel gave poor yields and control was difficult. This was expected since it is difficultly oxidized and reduced. Silver was similar to copper, as might be expected from the similarity of the two metals in other respects.

The form of these catalysts was not the same and a comparison of them may be open to question.

On the theoretical side, Norrish (20) has proposed a theory to explain the minor products of the reaction, and the kinetics of the reaction, more satisfactorily than Bone's Hydroxylation theory.

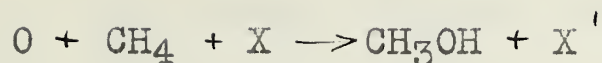
Norrish assumes as primary reactions:



a chain reaction, which may be terminated by either



of two ways:



where X is a third molecule.

From these equations it is seen that an increase in pressure favors the survival of methanol since a ternary collision is required for its formation. A reasonable explanation of the predominance of aldehydes at low pressures is given by the theory. Norrish also claims a satisfactory interpretation of the kinetic data on oxidations of hydrocarbons.

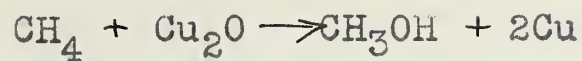
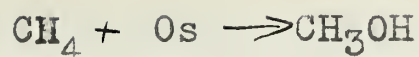
Boomer and Thomas (8) propose a theory for the mechanism of the reaction, combining features of both Bone's Hydroxylation theory, and of Norrish's chain reaction theory.

Evidence is offered for the occurrence of two primary reactions, (1) a surface reaction between methane and oxygen resulting in formation of methanol, and so desirable and (2) a homogeneous gas phase reaction, between oxygen and methane, resulting in formaldehyde and gases, and so undesirable.

For the surface reaction the oxygen may be absorbed on the catalyst surface, or combined with it:

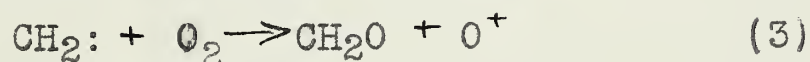


(1)

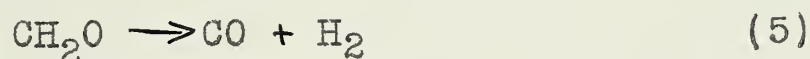
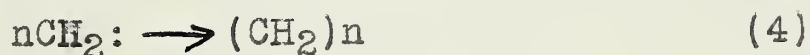


The methanol may survive or proceed to formaldehyde and formic acid, by Bone's mechanism through further oxidation. This reaction is required by Bone as the first stage in the oxidation of methane; it is also postulated in Norrish's theory, occurring as a chain breaker.

The homogeneous reaction is taken from Norrish's theory as:



a chain reaction that is broken by (1) above. The occurrence of the following reactions are postulated also:



all of which are known to occur in other work.

The present investigation is a continuation of that made by Boomer and Thomas. The optimum conditions of oxygen concentration, pressure and temperature, as found by them, have been used; and various metals in the same form used as catalysts, in an attempt to find the best catalyst for the survival of methanol.







The theory for the mechanism of the reaction, as proposed by them, has been used in an attempt to explain the observations made.



## EXPERIMENTAL METHODS

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### MATERIALS

Natural gas from the Viking field was used. The composition of this gas determined by ordinary combustion analysis was approximately:

|                        |       |
|------------------------|-------|
| $\text{CH}_4$          | 90.8% |
| $\text{C}_2\text{H}_6$ | 3.5%  |
| $\text{N}_2$           | 5.7%  |

Higher hydrocarbons such as propane were present in small amounts, and are included in the ethane figure. The gas was odorized with mercaptans and alkyl disulfides. The higher hydrocarbons and the sulfur compounds were removed by a method of purification, which is described in a later section.

The oxygen used was the commercial gas obtained from liquid air and compressed in steel cylinders.

Catalysts were used in two forms, viz., in the form of blocks about 3/16" square and 3/32" thick, and in the form of gauze. The reactor, which is described in detail in a later section, was tubular in shape, with a smaller tube, the thermocouple well, entering one end and



projecting half-way into the reactor. Rings of gauze were punched out of a sheet to fit snugly into the reactor and pass over the thermocouple well. These rings were packed into the reactor up to the level of the thermocouple well; the remainder of the reactor was packed with gauze discs. The gauze used was about 60 mesh, the diameter of the wire being about 0.006 inch.

For both forms of catalyst, the original metal was copper. To obtain other surfaces, the copper blocks, or discs and rings punched from copper gauze, were electroplated with the desired metal. In the form of blocks, copper and nickel surfaces were investigated; in the form of gauze, copper, silver, nickel and zinc surfaces were investigated.

The solutions used for electroplating were chosen from those suggested by Blum and Hogaboom (5). Their compositions and the operating conditions recommended are as follows:

For silver plating:

|                                | <u>Normality</u> | <u>Grams per liter of</u> |
|--------------------------------|------------------|---------------------------|
| AgCl                           | 0.27             | 39 (Solution)             |
| KC N                           | 0.84             | 55                        |
| K <sub>2</sub> CO <sub>3</sub> | 0.55             | 38                        |

Temperature----- Room temperature

Current density---- 0.3 to 0.9 amperes/  
dm.<sup>2</sup>





For nickel plating:

|  | <u>Normality</u> | <u>Grams per liter of solution</u> |
|--|------------------|------------------------------------|
| $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  | 0.75             | 105                                |
| $\text{NH}_4 \text{ Cl}$                   | 0.25             | 15                                 |
| $\text{Ni Cl}_2 \cdot 6\text{H}_2\text{O}$ | 0.13             | 15                                 |
| $\text{H}_3 \text{ BO}_3$                  | 0.25M            | 15                                 |

Temperature-----Room temperature

Current density--- over 1 ampere/dm<sup>2</sup>

For Zinc Plating:

|  | <u>Normality</u> | <u>Grams per liter of solution</u> |
|--|------------------|------------------------------------|
| $\text{Zn SO}_4 \cdot 7\text{H}_2\text{O}$ | 3.0              | 410                                |
| $\text{Na}_2 \text{ SO}_4$                 | 1.0              | 75                                 |
| $\text{Al Cl}_3 \cdot 6\text{H}_2\text{O}$ | 0.25             | 20                                 |

Temperature-----Room temperature

Current density--- 0.5 amperes/dm<sup>2</sup>

In all cases a platinum anode was used. The electroplate obtained was examined by means of a low power microscope, and the conditions adjusted if necessary, until a fine grained, adherent deposit was obtained.

At the points where the wires of the gauze crossed, plating did not occur and copper was left exposed.

The inside of the reactor also was copper plated, but



the total surface of copper was nevertheless slight,  
in comparison with the surface of the metal being in-  
vestigated.



## APPARATUS

### Gas Purification System

The method used was essentially that described by Boomer, Johnson and Thomas (9). The apparatus is shown in Figure 1. The process consisted essentially of cracking the higher hydrocarbons and sulfur compounds and then removing the undesired products of the reactions.

The flow of gas was controlled by observing the flowmeter, A, and manipulating the inlet stopcock. The gas was passed through a calcium chloride drier B, to a  $\frac{3}{4}$ " quartz tube C, heated to 825°C over a length of 12 inches, in which conversion of the ethane, heavier hydrocarbons and sulfur compounds in the natural gas to liquids, methane, olefines, hydrogen, and hydrogen sulfide occurred. The gas then passed through a glass wool filter D, to remove most of the tar, through a soda-lime tower E. to remove sulfur compounds, and to an activated charcoal absorber F, which removed the heavier hydrocarbons to a great extent. The gas was next scrubbed by sulfuric acid in the tower, G, holding about 400cc. concentrated sulfuric acid containing about 1% silver sulfate as catalyst. The acid was heated to 70°C with a gas burner. Continuous circulation of hot sulfuric





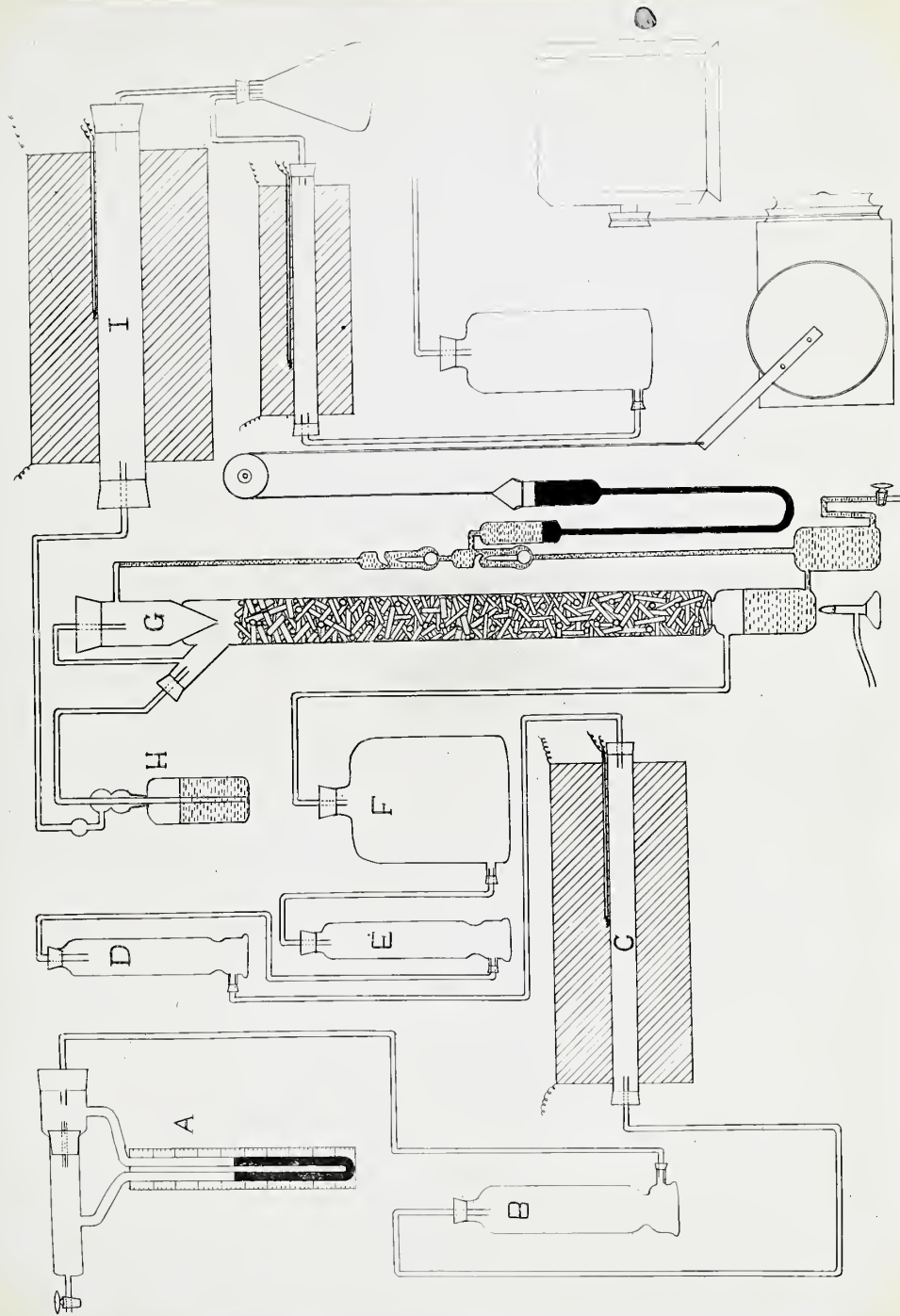


Figure 1.  
Gas Purification System.



acid was obtained by the glass and mercury pump G, as shown. The olefines were removed in this scrubber. The sodium hydroxide scrubber H, removed any sulfur dioxide produced by the reduction of the sulfuric acid in the scrubber or by oxidation of the sulfur compounds. The gas was then passed over 2 kilograms of copper oxide I, at 300°C., which oxidized the hydrogen and carbon monoxide to water and carbon dioxide. The bulk of the water was retained in the water trap, after which the gas was led through a smaller copper oxide tube at the same temperature, to remove the last traces of hydrogen. A soda lime tower removed carbon dioxide produced over the copper oxide.

The temperature of the pyrolysis furnace was maintained by means of an automatic controller. The temperatures of the copper oxide furnaces were controlled manually, through rheostats in the power supply.

No ethane nor heavier hydrocarbon was present in the gas purified in this manner. The gas did contain about 0.4% of olefines. This gas was used for some of the earlier experiments; for later experiments an attempt was made to decrease the olefines surviving, by modifying the apparatus. A second pyrolysis furnace, also heated to



825° C, followed by an activated charcoal absorber, was used before the gas entered the sulfuric acid scrubber. In this furnace some of the olefines was polymerized to heavier hydrocarbons, which were removed by the charcoal absorber. In addition, the gas was scrubbed by a second sulfuric<sup>acid</sup> scrubber of similar design, and placed directly after the first scrubber. With these additions the gas contained 0.1 to 0.2% olefines.

The purified gas was stored in water sealed gas holders. About 6% oxygen was added to the gas in the holders, from a cylinder of compressed oxygen gas. The mixture was pumped through a large steel bottle containing calcium chloride to remove water, and into the high pressure storage system.

The high pressure storage system was of such capacity that the pressure drop during an experiment was relatively small, about 50 pounds per square inch.

#### Reaction System

The reaction system is shown diagrammatically in Figure 2. From the high pressure storage the gas passed through two steel bottles A and B containing calcium chloride and activated charcoal respectively.





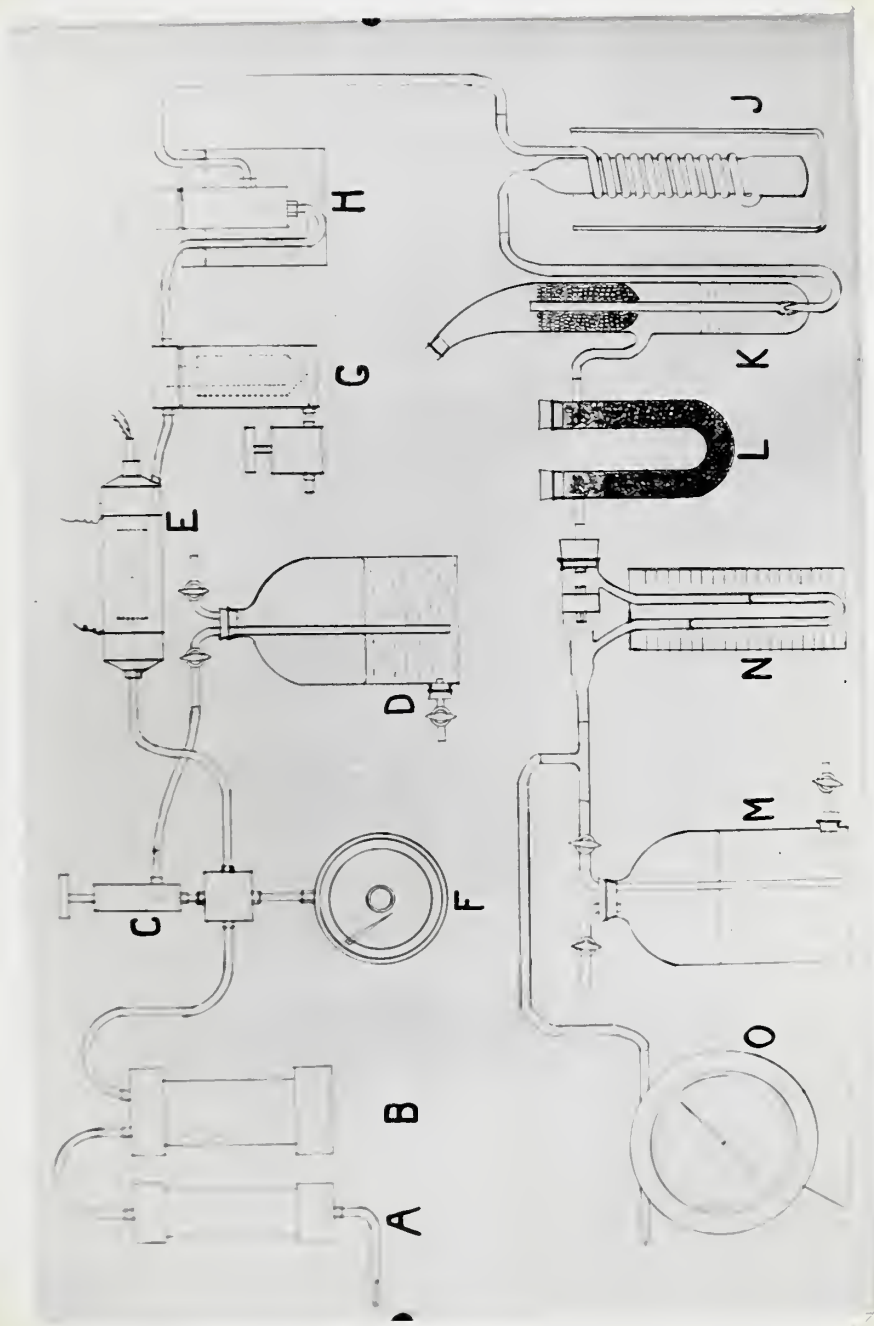


Figure 2.  
Reaction System.



The calcium chloride removed the last traces of water; the activated charcoal removed heavy hydrocarbons arising from oil vapor in the compressor, etc. A continuous sample of the in-let gas was drawn off through the heated expansion valve C, into the constant head sample bottle D. A record of the pressure during a run was obtained by means of the recording pressure gauge, F. This gauge was calibrated by comparison with a dead weight piston gauge. The gas mixture was passed through the reactor E, directly to the bottom of the water-cooled high pressure condenser G. The gases leaving the high pressure condenser were expanded to atmospheric pressure through the heated expansion valve H. The condenser G was chromium plated on the inside, the expansion valve was bronze, and all tubing after the reactor was copper to resist corrosion by the products of the reaction. The removal of methanol, formaldehyde formic acid, and water from the off-gas was completed by means of the ice condenser J, the water scrubber K, and the calcium chloride tube L. The flowmeter N, indicated the rate of flow of the off-gas. The total volume of gas passed was recorded by the calibrated wet test-meter O. A continuous sample of the off-gas was obtained in the constant head sample bottle M.



The reactor E, is shown in detail in Figure 3 . The main body, B, of the reactor was constructed of high nickel-chromium steel. All other parts were cut from chrome-molybdenum steel bar. The inlet tube A, and closure D, were cooled by running water in the tube H; the outlet tube, F, was similarly cooled by running water in the tube J. Both the closure D, and outlet tube F, were fitted with a lining of glass tubing. Consequently, the reacting gases were at reacting temperature only in the catalyst chamber or when in contact with glass. The interior surfaces of the reactor were copper-plated so that the reacting gases did not come in contact with ferrous surfaces. The reactor was heated electrically as shown. The temperature was obtained by means of a calibrated Iron-Constantan thermocouple placed in the thermocouple well, G. The temperature was measured by means of a potentiometric type of recording temperature controller which maintained the temperature constant to within two degrees. The catalyst was placed in the space E, of volume 12.7cc.





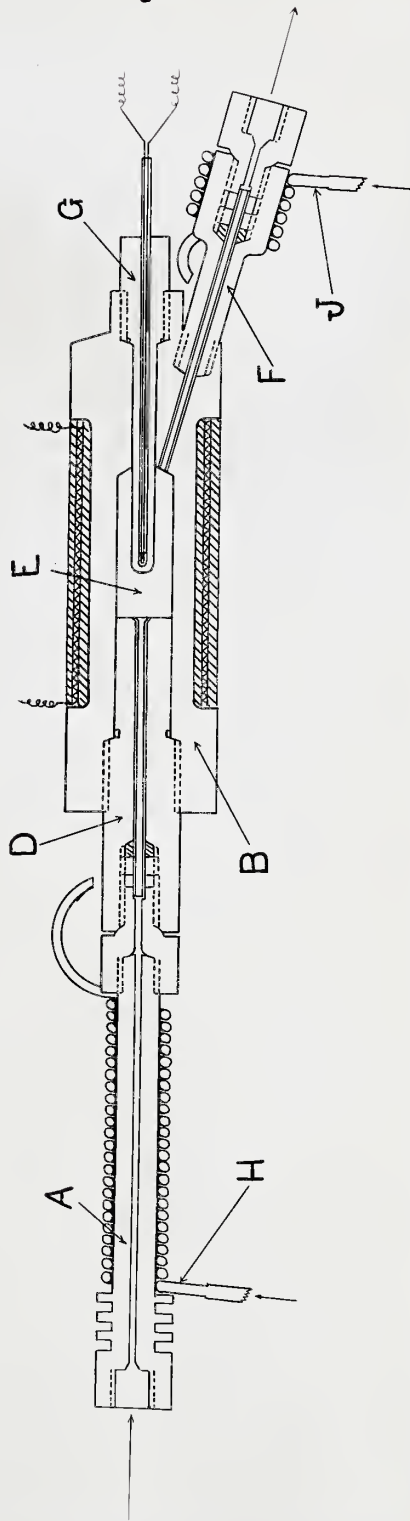


Figure 3.  
The Reactor.



## PROCEDURE

After a new catalyst had been placed in the reactor and the reacting system re-assembled, traces of oil were removed by drawing petrol ether through the inlet-gas sampling valve C, through the reacting system, and out through the valve at the bottom of the high pressure condenser G. Air was drawn through to remove the ether vapors.

The catalyst was then activated by alternate oxidation and reduction at the temperature at which the catalyst was to be investigated, viz., 450°C. Air was used to oxidize the catalyst; hydrogen and methanol vapor were used as a reducing agent.

In every experiment, after the pressure, temperature and rate of flow of off-gas had reached the steady state desired, the reaction was allowed to proceed for 20 to 30 minutes before the experimental observations were begun. This procedure was <sup>necessary</sup> to allow the catalyst to reach a steady state. Then the high pressure condenser was blown out; the gas meter was read, and the recovery system was connected to the expansion valve. The expansion valve was set with reference to the flow-meter. The inlet gas sample bottle was connected, and after the air had been swept from the recovery vessels, the off-gas



sample bottle was connected. The gas samples were collected over an aqueous solution of 20% sodium sulfate and 5% sulfuric acid. This solution did not dissolve significant amounts of any of the constituents of the gas sample. The rate of flow of this solution from the sample bottles, and consequently the rate of sampling during and experiment, was kept constant by means of a constant head aspirating device. In this manner representative average samples of inlet and off gases were obtained.

At the conclusion of an experiment, the volume of the off gas sample was observed, and added to the reading of the gas meter.

The liquid products were blown out of the high pressure condenser into the recovery vessels. The gain in weight of each item in the recovery system, and the total volume of off-gas were recorded. The efficiency of this recovery system had been demonstrated by Thomas (23).

The contents of the high pressure condenser, ice condenser and water scrubber were added to a 100ml. volumetric flask and made up to 100 ml. with distilled water. Aliquot portions were taken for the analysis of methanol, formaldehyde and formic acid.

Samples of the inlet gas and of the off gas were analysed.





## ANALYTICAL METHODS

All analyses were made in duplicate.

Gas analyses were carried out in a Burrell improved type of Bureau of Mines apparatus. Carbon dioxide was determined in potassium hydroxide solution, olefines in fuming sulfuric acid, and oxygen in potassium pyrogallate solution. Carbon monoxide and hydrogen were determined by combustion over copper oxide, and paraffin hydrocarbons by combustion with oxygen over a heated platinum filament.

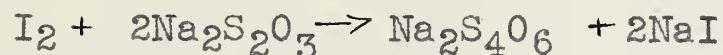
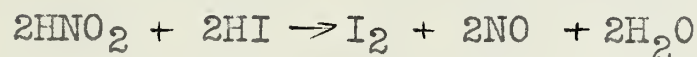
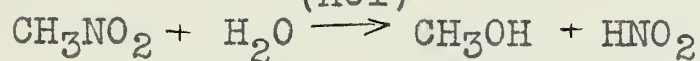
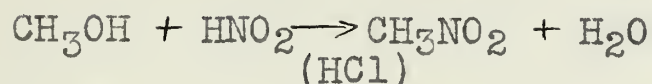
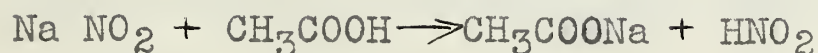
The analyses of liquid products were made according to the technique developed by Boomer and Broughton (6,10)

### Methyl Alcohol

Methyl alcohol was converted into methyl nitrite, which was carried by a stream of inert gas into an acidified solution of potassium iodide. Hydrolysis of the methyl nitrite took place, the nitrous acid liberated reacting with the hydriodic acid, forming free iodine. The iodine was then titrated against a standard solution of 0.1N sodium thiosulfate. Calculations were made on the basis that one molecular weight of sodium thiosulfate is equivalent to one molecular weight of methyl alcohol,



as shown by the following equations:



A five ml. aliquot of the diluted condensate was used for this determination.

### Formaldehyde

Formaldehyde was determined by Romijn's cyanide method (22) which is specific for this compound. A 10 ml. aliquot of the diluted condensate was treated with an excess of 0.1N. potassium cyanide solution. A soluble addition product of formaldehyde and potassium cyanide forms, one molecule of formaldehyde combining with one molecule of cyanide. The excess potassium cyanide was determined as follows: After the sample had been treated with potassium cyanide it was washed into a flask containing a measured amount of 0.1N. silver nitrate solution. The excess cyanide precipitates as AgCN. This precipitate was filtered off, and the excess silver nitrate in the filtrate determined by titration against 0.1N. potassium thiocyanate, using ferric alum indicator. From the



above data, the amount of potassium cyanide which had been removed by formaldehyde could be calculated.

#### Formic Acid

A 10 ml. aliquot of the diluted condensate was used to determine formic acid. An excess of 0.05N. sodium hydroxide was added, and the sample heated to boiling to expel carbon dioxide. At the same time if any copper formate was present, a precipitate of copper hydroxide was obtained. This was filtered off, and the filtrate was back titrated with 0.05N. sulfuric acid.

The pipettes and burettes used in the above determinations were calibrated, and the solutions which were likely to change in concentration, such as sodium thiosulfate and potassium cyanide, were checked from time to time.





## EXPERIMENTAL RESULTS

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The primary purpose of this investigation was an endeavor to find a better catalyst than copper blocks for the production of methanol by the direct oxidation of methane under pressure. The optimum conditions of temperature, pressure and oxygen concentration as found by Boomer and Thomas (8) were used in all experiments. These optimum conditions were determined using copper blocks as catalyst; they may not necessarily be the optimum conditions for the other catalysts examined. The present investigation however, attempts only a preliminary survey of some possible catalysts.

Surfaces of copper, silver, nickel and zinc were investigated in the form of gauze. In all cases copper surfaces were present however, since the walls of the reactor were copper plated. Also, some copper was left exposed on the gauze when it was electroplated with the metal being investigated.

A series of experiments was made using copper blocks, in order to compare the efficiency of the gauze form of catalyst with the block form.

Nickel also was examined in the form of blocks, as



well as gauze.

All calculations of yields based on 100 litres of inlet gas at N.T.P. The ratio of the volume of inlet gas to off-gas varied so that yields cannot be compared on the basis of the off-gas volume. Since the volume of in-gas was not measured directly, the volume conversion factor between the inlet gas and the off-gas was found by using a carbon balance, as described by Broughton (10). The total carbon content of the liquid products and the off-gas was calculated. From this quantity, and the carbon content of the in-gas, the volume of in-gas which had entered the reactor was calculated. This method assumes of course, that all the carbon entering the system was accounted for in the products. The analytical methods were confirmed by Boomer and Thomas (7) by ultimate analysis for carbon and hydrogen, and a carbon balance was believed to be reliable. However, they found that on the basis of a carbon balance the other elements involved did not show a good balance. The nitrogen balance and the hydrogen balance were fairly good, but the oxygen balance showed very great discrepancies. The same errors are present in this investigation. It has also been reported by Wiezewitch and Frolich (25). No explanation has been found.



Runs 9, 10, 12, 13 and 14 show the results using copper blocks as catalyst. For the same conditions Boomer and Thomas (8) obtained yields of about 60% methanol on the basis of carbon oxidized. From the low yields of Runs 9 and 10 it was suspected that the catalyst was poisoned. Therefore, the reaction system was cleaned with petrol ether and the catalyst was reactivated. The yield was increased somewhat, as shown by Runs 12, 13 and 14, but was still below that obtained by Boomer and Thomas. It is suggested that the relatively high concentration of olefines in the in-gas may act as a poison. In subsequent experiments, gas containing less olefines was used. These experiments were carried out at different rates of flow. It is apparent that within the range examined, space velocity did not exert any significant effect on the yield of methanol.

Runs 15 and 16 were made with the reactor packed with copper gauze. The survival of methanol was less than for the copper blocks. The catalyst was re-activated in an attempt to raise the yield of methanol. The yield was improved, as shown by Runs 18, 19 and 20, and appeared to be steady. The yield was still considerably below the yield using copper blocks. This was not expected.







| Experiment No                                   | 9                                       | 10        | 12        | 13        | 14        |
|---|---|-----------|-----------|-----------|-----------|
| Catalyst  | Cu blocks                               | Cu blocks | Cu blocks | Cu blocks | Cu blocks |
| Temperature, C                                  | 450                                     | 450       | 450       | 450       | 450       |
| Pressure, atmospheres                           | 180                                     | 182       | 200       | 183       | 186       |
| Off-gas flow, litres/min.                       | 0.69                                    | 1.03      | 1.10      | 0.38      | 1.22      |
| In-gas analysis:                                |   |           |           |           |           |
| C <sub>2</sub> H <sub>4</sub>                   | 0.45                                    | 0.45      | 0.45      | 0.45      | 0.40      |
| O <sub>2</sub>                                  | 5.5                                     | 5.6       | 5.8       | 5.8       | 5.7       |
| CH <sub>4</sub>                                 | 87.8                                    | 88.4      | 87.7      | 87.0      | 87.8      |
| N <sub>2</sub>                                  | 6.25                                    | 5.55      | 6.05      | 6.75      | 6.1       |
| Off-gas analysis:                               |   |           |           |           |           |
| CO <sub>2</sub>                                 | 1.25                                    | 1.20      | 1.30      | 1.55      | 1.30      |
| C <sub>2</sub> H <sub>4</sub>                   | 0.15                                    | 0.25      | 0.1       | 0.15      | 0.0       |
| O <sub>2</sub>                                  | 0.20                                    | 0.20      | 0.2       | 0.3       | 0.3       |
| H <sub>2</sub>                                  | 2.7                                     | 2.0       | 1.2       | 0.45      | 0.65      |
| CO  | 1.5                                     | 1.5       | 0.65      | 0.25      | 0.4       |
| CH <sub>4</sub>                                 | 87.2                                    | 87.8      | 88.9      | 89.6      | 89.7      |
| N <sub>2</sub>                                  | 6.4                                     | 7.05      | 7.65      | 7.7       | 7.65      |
|   | <i>C<sub>2</sub>H<sub>6</sub> = 0.5</i> |           |           |           |           |
| <u>Volume In-gas</u>                            |   |           |           |           |           |
| <u>Volume Off-gas</u>                           | 1.05                                    | 1.04      | 1.04      | 1.06      | 1.05      |
| Condensate, gms./100 litres<br>in-gas at N.T.P. |   |           |           |           |           |
| Total   | 6.74                                    | 6.44      | 5.90      | 5.90      | 6.41      |
| CH <sub>3</sub> OH                              | 1.803                                   | 1.900     | 1.845     | 1.739     | 1.844     |
| CH <sub>2</sub> O                               | 0.0330                                  | 0.0220    | 0.0245    | 0.0417    | 0.354     |
| HCOOH   | 0.0440                                  | 0.0320    | 0.0281    | 0.0240    | 0.0315    |
| H <sub>2</sub> O                                | 4.86                                    | 4.49      | 4.00      | 4.10      | 4.50      |
| Alcohol in condensate, %                        | 26.8                                    | 29.5      | 31.3      | 29.5      | 28.8      |
| Total carbon oxidized, %                        | 4.46                                    | 4.45      | 3.60      | 3.33      | 3.54      |
| Yields as percent total<br>carbon burned to:    |   |           |           |           |           |
| CH <sub>3</sub> OH                              | 31.9                                    | 33.5      | 40.5      | 41.7      | 43.7      |
| CH <sub>2</sub> O                               | 0.62                                    | 0.40      | 0.59      | 0.61      | 0.90      |
| HCOOH   | 0.54                                    | 0.39      | 0.43      | 0.70      | 0.52      |
| Total   | 33.06                                   | 34.29     | 41.70     | 43.01     | 45.12     |



| Experiment No.                                  | 15       | 16       | 18       | 19       | 20       |
|---|----------|----------|----------|----------|----------|
| Catalyst  | Cu gauze | Cu gauze | Cu gauze | Cu gauze | Cu gauze |
| Temperature, C.                                 | 450      | 450      | 450      | 450      | 450      |
| Pressure, atmospheres                           | 177      | 172      | 174      | 177      | 176      |
| Off-gas flow, litres/min.                       | 1.10     | 1.10     | 1.10     | 1.10     | 1.14     |
| In gas analysis:                                |          |          |          |          |          |
| $C_2H_4$  | 0.2      | 0.2      | 0.1      | 0.1      | 0.15     |
| $O_2$   | 6.3      | 6.0      | 6.0      | 6.1      | 5.7      |
| $CH_4$  | 86.7     | 86.7     | 85.0     | 83.9     | 85.3     |
| $N_2$   | 6.8      | 7.1      | 8.9      | 9.9      | 8.85     |
| Off-gas analysis:                               |          |          |          |          |          |
| $CO_2$  | 1.70     | 1.85     | 1.60     | 1.50     | 1.50     |
| $C_2H_4$  | 0.2      | 0.1      | 0.0      | 0.0      | 0.0      |
| $O_2$   | 0.2      | 0.3      | 0.3      | 0.3      | 0.3      |
| $H_2$   | 0.55     | 0.60     | 1.0      | 1.1      | 1.0      |
| $CO$  | 0.90     | 0.45     | 0.7      | 0.7      | 0.6      |
| $CH_4$  | 89.0     | 89.6     | 87.6     | 87.6     | 88.0     |
| $N_2$   | 7.45     | 7.1      | 8.8      | 8.8      | 7.6      |
| <u>Volume In-gas</u>                            |          |          |          |          |          |
| <u>Volume Off-gas</u>                           | 1.07     | 1.07     | 1.07     | 1.08     | 0.06     |
| Condensate, gms./100 litres<br>in-gas at N.T.P. |          |          |          |          |          |
| Total   | 7.08     | 6.58     | 6.41     | 5.66     | 5.81     |
| $CH_3OH$  | 1.019    | 1.019    | 1.330    | 1.321    | 1.148    |
| $CH_2O$   | 0.0864   | 0.0859   | 0.0479   | 0.0484   | 0.0494   |
| $HCOOH$   | 0.0221   | 0.0255   | 0.0332   | 0.0310   | 0.0340   |
| $H_2O$  | 5.95     | 5.45     | 5.00     | 4.26     | 4.58     |
| Alcohol in condensate, %                        | 14.4     | 15.5     | 20.8     | 23.3     | 19.8     |
| Total carbon oxidized, %                        | 3.70     | 3.37     | 3.68     | 3.59     | 3.31     |
| Yields as percent total<br>carbon burned to:    |          |          |          |          |          |
| $CH_3OH$  | 22.1     | 24.3     | 29.7     | 30.6     | 28.4     |
| $CH_2O$   | 2.0      | 2.2      | 1.1      | 1.2      | 1.5      |
| $HCOOH$   | 0.34     | 0.41     | 0.52     | 0.50     | 0.59     |
| Total   | 24.44    | 26.91    | 31.32    | 32.30    | 30.29    |



According to the theory for the course of the reaction proposed by Boomer and Thomas (8), methanol is formed by a surface reaction, and the homogeneous gas phase reaction is detrimental, leading to carbon oxides and water. The weight of copper used as catalyst form of blocks was 56 grams, the gauze catalyst weighed only 38 grams. Hence there was more free space in the reactor when gauze was used, and therefore, more opportunity for detrimental homogeneous gas phase reactions. Blocking off part of the reactor with solid discs, thereby decreasing the free space might increase the survival of methanol.

It is also probable that the larger surface area of the gauze promotes more rapid reaction, and consequently there is more heat liberated per unit of mass of copper, than is the case with copper blocks. Therefore, the conduction of the heat of the reaction away from the surface is probably not as rapid with the gauze as with the blocks, and consequently the surface temperature may be high. A lack of temperature control is probably responsible in part, for the decreased survival of methanol when gauze was used.

The conclusion must be that gauze is not the best form of catalyst. Catalysts should be compared under optimum conditions, differences in their behavior being







most marked under the most favorable conditions. Under unfavorable conditions all of the catalysts may be expected to approach the same inefficient state. Nevertheless, the results obtained using one of the metals in the form of gauze should be comparable with the other investigations made under the same conditions. A rating of the metals as catalysts is probably justified.

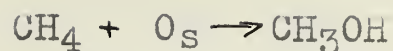
Runs 21, 22 and 23 were made using the silver gauze catalyst in the reactor. The yield of methanol was lower than was obtained using copper in the same form. Boomer and Broughton (6) and Boomer and Thomas (8) found silver to be as good a catalyst as copper. However, in both of these previous investigations, the form of the silver catalyst was not the same as the copper catalyst with which it was compared. In view of the fact that the form of the catalyst appears to exert considerable influence on the survival of methanol, comparison of silver and copper in the previous investigations is probably not justified.

For the surface reaction Boomer and Thomas (8) consider that, oxygen may be absorbed on the catalyst surface or combined with the catalyst, for example, as euprous oxide------. The surface reaction may be written as: \_



| Experiment No.                                  | 21       | 22       | 23       | 27       | 28       | 29       |
|---|----------|----------|----------|----------|----------|----------|
| Catalyst  | Ag gauze | Ag gauze | Ag gauze | Zn gauze | Zn gauze | Zn gauze |
| Temperature, C                                  | 450      | 450      | 450      | 450      | 450      | 450      |
| Pressure, atmospheres                           | 176      | 179      | 179      | 182      | 181      | 190      |
| Off-gas flow, litres/min.                       | 1.09     | 1.06     | 1.10     | 1.10     | 1.10     | 1.07     |
| In gas analysis:                                |          |          |          |          |          |          |
| C <sub>2</sub> H <sub>4</sub>                   | 0.15     | 0.2      | 0.2      | 0.2      | 0.2      | 0.2      |
| O <sub>2</sub>                                  | 5.8      | 5.9      | 5.9      | 5.8      | 5.8      | 5.8      |
| CH <sub>4</sub>                                 | 84.9     | 84.6     | 84.6     | 84.6     | 84.7     | 84.8     |
| N <sub>2</sub>                                  | 9.15     | 9.3      | 9.3      | 9.4      | 9.3      | 9.2      |
| Off-gas analysis:                               |          |          |          |          |          |          |
| CO <sub>2</sub>                                 | 2.0      | 1.7      | 1.7      | 1.9      | 2.2      | 2.5      |
| C <sub>2</sub> H <sub>4</sub>                   | 0.0      | 0.05     | 0.1      | 0.05     | 0.05     | 0.05     |
| O <sub>2</sub>                                  | 0.2      | 0.25     | 0.3      | 0.3      | 0.3      | 0.3      |
| H <sub>2</sub>                                  | 0.65     | 2.2      | 2.4      | 3.0      | 2.6      | 3.0      |
| CO  | 0.55     | 0.8      | 0.9      | 0.8      | 0.6      | 0.5      |
| CH <sub>4</sub>                                 | 89.2     | 87.1     | 86.7     | 87.1     | 87.1     | 86.9     |
| N <sub>2</sub>                                  | 7.4      | 7.9      | 7.9      | 6.85     | 7.15     | 6.75     |
| Volume In-gas                                   |          |          |          |          |          |          |
| Volume Off-gas                                  | 1.09     | 1.07     | 1.05     | 1.06     | 1.06     | 1.06     |
| Condensate, gms./100 litres<br>in-gas at N.T.P. |          |          |          |          |          |          |
| Total   | 5.52     | 5.21     | 5.12     | 4.65     | 4.31     | 3.77     |
| CH <sub>3</sub> OH                              | 1.010    | 0.9638   | 0.8958   | 0.7001   | 0.5696   | 0.0630   |
| CH <sub>2</sub> O                               | 0.0319   | 0.0430   | 0.0368   | 0.0094   | 0.0130   | 0.0092   |
| HCOOH   | 0.0361   | 0.0357   | 0.0288   | 0.0320   | 0.0313   | 0.0026   |
| H <sub>2</sub> O                                | 4.44     | 4.16     | 4.16     | 3.91     | 3.70     | 3.70     |
| Alcohol in condensate, %                        | 18.3     | 18.5     | 17.5     | 15.1     | 13.2     | 1.67     |
| Total carbon oxidized, %                        | 3.68     | 3.62     | 3.69     | 3.59     | 3.59     | 3.39     |
| Yields as percent total<br>carbon burned to:    |          |          |          |          |          |          |
| CH <sub>3</sub> OH                              | 22.5     | 22.0     | 20.0     | 16.1     | 13.0     | 1.53     |
| CH <sub>2</sub> O                               | 0.76     | 1.05     | 0.88     | 0.23     | 0.32     | 0.24     |
| HCOOH   | 0.56     | 0.57     | 0.45     | 0.51     | 0.50     | 0.43     |
| Total   | 23.82    | 23.62    | 21.33    | 16.84    | 13.82    | 2.20     |





On this basis, silver and copper should have similar properties as catalysts, since both are easily oxidized and reduced. However, silver can dissolve more oxygen than copper, and it is possible that the increased concentration of oxygen in the surface promotes further oxidation, resulting in carbon oxides and water. The lower yields with silver in the present investigation may be explicable on this basis.

Using the same principles, an explanation may be offered for the low yields observed with the zinc catalyst, used in Runs 27, 28 and 29. Zinc does not dissolve appreciable amounts of oxygen and very little activated oxygen will be available for reaction from this source. Furthermore zinc oxide when formed is stable. Reversible oxidation--reduction of zinc does not occur under the conditions of these experiments. Consequently, the mechanism proposed for the production of methanol is not possible and if it is the correct mechanism, little or no methanol should be produced with this catalyst.

It will be observed that in the three runs made with zinc, Numbers 27, 28 and 29, the yields of methanol were







respectively 16.0%, 13.0% and 1.5%. It is suggested that during the first two runs the oxidation of zinc was not completed but that late in the second run or early in the third, the zinc had become completely oxidized. In the first two runs, the zinc surfaces still present may have promoted methanol formation. In the third run, only a zinc oxide surface was present, which was inert, or promoted only complete oxidation to carbon oxides and water.

When removed from the reactor, the catalyst was a dark brown color. The deposit present was completely soluble in 2 N. HCl, indicating that it was not carbon, and leaving the possibility that it was zinc oxide, perhaps mixed with copper or copper oxide.

In all other cases, the catalyst when removed from the reactor was quite bright. When gauze was used, there were "ripple" marks on the layers of the gauze near the gas entry to the reactor, such as might be caused by the corrosion of a liquid. It is possible that most of the reaction occurred in this part of the reactor.

The results of the investigations of the nickel catalysts are particularly interesting. Runs 24, 25 and 26 offer a comparison of nickel in the form of gauze with



other catalysts. It will be observed that the yield of methanol is slightly higher than for copper gauze. (Runs 18, 19 and 20). Runs 30 and 31 were made with nickel blocks. These were obtained by electroplating the identical copper blocks used in Runs 12, 13 and 14. Comparing the two forms of copper and nickel, these catalysts are in order of effectiveness:- copper blocks, nickel blocks, nickel gauze and copper gauze. The range of yields as per cent of carbon oxidized is from over 43% to 30%. The two gauze catalysts gave very similar yields suggesting that the form of catalyst is the predominating influence. The specific influence of the metal is subordinated, as has been discussed above, by the detrimental effect which results from too much surface per unit of mass. With blocks, a better form of catalyst, the specific influence of the metal is more apparent.

Nickel undergoes oxidation and reduction with an ease which is intermediate between copper and zinc. Furthermore, the overvoltage of oxygen on nickel, being quite low, suggests that the metal is a fair solvent for the gas. In these respects, it appears to satisfy the conditions favoring methanol production almost as well as does copper. For this reason it is not surprising that it is quite similar to copper as a catalyst.



| Experiment No.                                 | 24       | 25       | 26       | 30        | 31        |
|--|----------|----------|----------|-----------|-----------|
| Catalyst                                       | Ni gauze | Ni gauze | Ni gauze | Ni blocks | Ni blocks |
| Temperature, C                                 | 450      | 450      | 450      | 450       | 450       |
| Pressure, atmospheres                          | 177      | 182      | 184      | 185       | 188       |
| Off-gas flow, litres/min                       | 1.09     | 1.06     | 1.07     | 1.07      | 1.07      |
| In-gas analysis:                               |          |          |          |           |           |
| C <sub>2</sub> H <sub>4</sub>                  | 0.2      | 0.2      | 0.2      | 0.2       | 0.2       |
| O <sub>2</sub>                                 | 5.8      | 5.8      | 5.8      | 5.8       | 5.8       |
| CH <sub>4</sub>                                | 84.7     | 84.7     | 84.6     | 84.6      | 84.7      |
| N <sub>2</sub>                                 | 9.3      | 9.3      | 9.4      | 9.4       | 9.3       |
| Off-gas analysis:                              |          |          |          |           |           |
| CO <sub>2</sub>                                | 1.6      | 1.4      | 1.5      | 1.15      | 1.3       |
| C <sub>2</sub> H <sub>4</sub>                  | 0.05     | 0.05     | 0.05     | 0.05      | 0.05      |
| O <sub>2</sub>                                 | 0.3      | 0.25     | 0.3      | 0.3       | 0.3       |
| H <sub>2</sub>                                 | 1.7      | 1.6      | 1.7      | 1.5       | 1.4       |
| CO   | 0.8      | 0.8      | 0.9      | 1.2       | 1.1       |
| CH <sub>4</sub>                                | 87.3     | 87.8     | 87.0     | 87.5      | 87.6      |
| N <sub>2</sub>                                 | 8.25     | 8.1      | 8.55     | 8.30      | 8.25      |
| <u>Volume In-gas</u>                           |          |          |          |           |           |
| <u>Volume Off-gas</u>                          | 1.07     | 1.08     | 1.07     | 1.08      | 1.07      |
| Condensate, gms./100 litres<br>in-gas at N.T.P |          |          |          |           |           |
| Total  | 6.30     | 6.00     | 6.11     | 7.28      | 6.79      |
| CH <sub>3</sub> OH                             | 1.538    | 1.549    | 1.494    | 1.755     | 1.695     |
| CH <sub>2</sub> O                              | 0.0178   | 0.0174   | 0.0180   | 0.0621    | 0.0532    |
| HCOOH  | 0.0439   | 0.0421   | 0.0404   | 0.0328    | 0.0298    |
| H <sub>2</sub> O                               | 4.70     | 4.39     | 4.56     | 5.43      | 5.01      |
| Alcohol in condensate, %                       | 24.3     | 25.8     | 24.5     | 24.1      | 25.0      |
| Total carbon oxidized, %                       | 3.94     | 3.72     | 3.92     | 4.09      | 4.09      |
| Yields as percent total<br>carbon burned to:   |          |          |          |           |           |
| CH <sub>3</sub> OH                             | 32.1     | 34.3     | 31.4     | 35.3      | 34.1      |
| CH <sub>2</sub> O                              | 0.40     | 0.41     | 0.40     | 1.3       | 1.1       |
| HCOOH  | 0.64     | 0.65     | 0.59     | 0.46      | 0.42      |
| Total  | 33.14    | 35.36    | 32.39    | 37.06     | 35.62     |







Nickel appears to promote more reaction than any of the other catalysts in that more methane is attacked to form partially oxidized products. In both gauze and block form, the percentage of carbon oxidized is higher, for the same initial oxygen concentration, than with the other catalysts. While more carbon is oxidized over copper blocks in experiments 9 and 10, it must be borne in mind that the yields of methanol are very low. Nickel shows for equal amounts of carbon oxidized a greater production of useful products than either silver or zinc and is equal to or better than copper. Comparing experiments 14, using copper blocks, and 30, using nickel blocks, 1.51% and 1.52% respectively, of the carbon entering the system is recovered as useful products. The total carbon oxidized is respectively 3.34% and 4.09%. The production of carbon monoxide and hydrogen is relatively large over nickel; this result might be expected in view of the well-known activity of nickel in promoting reactions like the water gas and related equilibria. It is possible that the nickel catalyst may be modified to promote formation of methanol from this carbon monoxide. Certainly, there is a possibility of great improvement in the action of nickel and the possibility of a greater yield than with copper. It appears to be worthy of further study.



Since it is more active than copper, the optimum temperature for it may be below the optimum for copper. The effect of oxygen concentration, pressure and rate of flow may also be different. A knowledge of the effect of these variables on the yield might aid in explaining the similarity of the two forms of nickel, whereas a difference was observed with copper. In any case, under its optimum conditions nickel might be expected to be considerably better than copper. The conditions chosen for the series of experiments reported were those most favorable for the copper catalyst, and will not necessarily be the best conditions for nickel. Further studies of nickel, and possibly of alloys of nickel and copper, should be made. The promoting effect of one of these metals on the other may result in better yields than that obtainable by either metal alone.



## C O N C L U S I O N S

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The gauze form of catalyst has been compared with massive blocks for copper and for nickel. The massive blocks appear to be somewhat superior to gauze for the conditions under which the comparison was made.

Nickel, silver, zinc and copper have been compared as catalysts in the form of gauze. None was found to be a good catalyst; nickel was best, with copper nearly as good. In the form of blocks, nickel and copper have been compared. Copper was somewhat better.

Although under the conditions examined none of the catalysts is good, it is believed that nickel is worthy of further investigation. It was superior to the other catalysts in promoting the most extensive oxidation of carbon.





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R E F E R E N C E S

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